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OKLAHOMA UNIV NORMAN DEPT OF CHEMISTRY
A REINVESTIGATION OF THE CLAIM THAT STANNOCENE AND H5 -CYCLO-
MAY 81 T S DORY, J J ZUCKERMAN, C D HOFF
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A Reinvestigation of the Claim that Stannocene and h^5 -
Cyclopentadienyltricarbonyltungsten Hydride Form
Bis-(h^5 -cyclopentadienyltricarbonyltungsten)tin(II).

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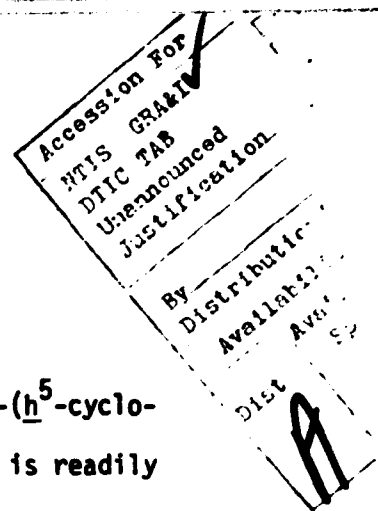
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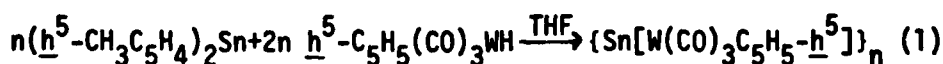
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Summary

Bis-(η^5 -cyclopentadienyl)tin(II), and η^5 -cyclopentadienyltricarbonyltungsten hydride form tris-(η^5 -cyclopentadienyl)tricarbonyltungsten)tin(IV) hydride which is readily halogenated by the halocarbon solvents used to form the corresponding tin(IV) halides rather than the bis-(η^5 -cyclopentadienyl)tricarbonyltungsten)tin(II) product previously claimed.

Of the seven categories of tin(II) compounds which can be potentially distinguished by tin-119m Mössbauer spectroscopy,¹ one category, embracing tin(II) compounds with electropositive ligands, contains a single member, namely [η^5 -C₅H₅(CO)₃W]₂Sn.² This vermilion solid was obtained by recrystallization from methylene chloride of the product from the exothermic reaction of bis-(η^5 -methylcyclopentadienyl)tin(II) and η^5 -cyclopentadienyltricarbonyltungsten hydride:



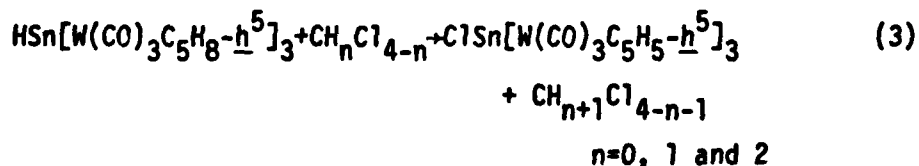
The product gave apparently satisfactory analyses as formulated [Calcd. for C₁₆H₁₀O₆SnW₂: C, 24.5; H, 1.3%. Found: C, 24.9; H, 1.7%]. The tin-119m Mössbauer spectrum was a doublet with Isomer Shift (I.S.) = 2.08 ± 0.05 and Quadrupole Splitting (Q.S.) = 2.05 ± 0.10 mm s⁻¹. The magnitude of the I.S. value, which lies outside the tin(II) range,³ was at first attributed to the auto-

oligomerization well-known in tin(II) chemistry which gives tin(IV) species with tin-tin bonds. A subsequent report gave the results of an osmometric molecular weight determination in chloroform as 1007 vs. the calculated value of 785 for the monomer ($n = 1$) product depicted in Eq. 1. The mass spectrum was interpreted in terms of polyisotopic $[P-nCO]^+$ ($n = 4-6$) and $[P-C_5H_5-mCO]^+$ ($m = 5,6$) fragments.⁴

The action of stannocene on analogous molybdenum carbonyl hydrides is complex, yielding a tris-(molybdenum carbonyl)tin (IV) hydride product. In addition, the tin-hydrogen bonds in this series are readily halogenated by halocarbons under mild conditions.⁵ We find that the product from the action of stannocene on \underline{h}^5 -cyclopentadienyltricarbonyltungsten hydride is tris-(\underline{h}^5 -cyclopentadienyltricarbonyltungsten)tin(IV) hydride:



and not the bis-(\underline{h}^5 -cyclopentadienyltricarbonyltungsten)tin previously claimed. Further, treatment with methylene chloride, chloroform or carbon tetrachloride produces a deep red solution containing tris-(\underline{h}^5 -cyclopentadienyltricarbonyltungsten)tin(IV) chloride:⁶



It is this product that is formed by the procedure used in reference 2. The analytical data reported there fit this formulation [Calcd.: C, 24.98; H, 1.30%] better, the molecular weight of 1153 fits the measured value within experimental error,⁴ and the Mössbauer parameters are those expected from a tris-transition metal-substituted tin(IV) chloride.^{3,7-9} An absorption band is found at 352 cm^{-1} in the infrared which arises from the $\nu(\text{Sn-Cl})$ mode, and the $\delta(\text{Sn-Cl})$ is found in the Raman at 151 cm^{-1} . Titration of the starting materials in an nmr tube confirmed the stoichiometry of Eq. 3. No signals arising from intermediates were observed, and the tris-compound is the sole tin-containing product, even in an excess of stannocene.

Treatment of the hydride with 1,3-dibromopropane or methylene bromide, or methyl iodide yields the tris(η^5 -cyclopentadienyltricarbonyltungsten)tin bromide and iodide, respectively.

The properties of the four tris-(η^5 -cyclopentadienyltricarbonyltungsten)tin products are listed in Table 1.

Thus the synthesis of a tin(II) compound with electropositive ligands¹ is still awaited.

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Table 1. Properties of $\text{ESn}[\text{W}(\text{CO})_3\text{C}_5\text{H}_5\text{-h}^5]_3$

	$\text{E} = \text{H}^{\underline{\text{a}}}$	$\text{Cl}^{\underline{\text{b}}}$	$\text{Br}^{\underline{\text{b}}}$	$\underline{\text{I}}^{\underline{\text{b}}}$
Yield	72	86	68	83
m.p. 196-203°d.	196-203°d	212°d. ^{<u>c</u>}	210-214°d.	185-189°d.
^1H nmr (ppm)	4.93 ^{<u>d</u>}	5.02	5.03	5.03
Infrared $\nu(\text{CO})(\text{cm}^{-1})$	2016(m) ^{<u>e</u>} 2000(m)	2025(s) ^{<u>f,g</u>} 2005(s)	2026(sh) ^{<u>f</u>} 2011(m)	2028(sh) ^{<u>f</u>} 2018(m)
	1970(s) 1920(s) 1900(s)	1985(m) 1948(m) 1930(s)	1985(s) 1920(s) 1888(sh)	1982(s) 1912(s) 1890(sh)
Mössbauer (mm s^{-1})				
I.S.	1.79±0.02	1.98±0.02	1.99±0.01	1.95±0.01
Q.S.	---	1.86±0.03	1.87±0.01	1.81±0.04

^aSatisfactory analyses were obtained for C, H, Sn and W.

^bSatisfactory analyses were obtained for C, H and the halogen.

^cLit. 198°. ⁶

^d $\delta\text{H-Sn} = 5.01$ ppm; $|^1J(^{117,119}\text{Sn}-^1\text{H})| = 2066$ Hz.

^eIn THF.

^fIn CH_2Cl_2 .

^gReported as 2012(w,sh), 2004(m), 1982(s), 1968(s), and 1913(s,sh), 1894(vs), 1880(s,sh) and 1866(m) in ref. 2 for the solid, and as 2015(m), 2005(m), 1979(m), 1948(m), 1922(s) and 1905(s,sh) in dichloromethane solution.

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